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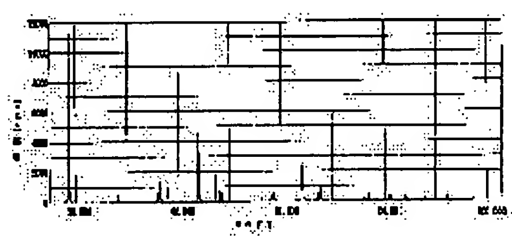
(54) NONAQUEOUS ELECTROLYTIC SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolytic secondary battery with good storage characteristic, in which manganese elution does not occur even at a temperature beyond room temperature in particular, while maintaining a high capacity by using a lithium manganese oxide with its good crystalline and a battery internal impedance is not increased.



SOLUTION: In a nonaqueous electrolytic secondary battery, a material of a spinel-based lithium manganese oxide which is represented by Li[Lix Mn2-x]O4 (where $0\leq x\leq 0.18$), and in X-ray diffraction pattern in which Cu-Kα1 is a used as a linear source, it has at least a diffraction peak, when $2\theta=36.2\pm0.2°$ (A) and $2\theta=44.0\pm0.2°$ (B), a half width of this X-ray diffraction peak is 0.1 ± 0.05, and that refraction peak strength ratio (B/A) which is 0.9 or more or 1.3 or less is used as a positive electrode.

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JAPANESE [JP,10-241685,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention improves the increment in internal impedance of the nonaqueous electrolyte rechargeable battery which used the lithium manganic acid ghost as positive active material.
[Description of the Prior Art] Small [of a device] and lightweight-ization are advanced at a surprising speed by development of electronic technology in recent years. For this reason, mobile computing devices, such as mobile communication equipment and a portable computer, are beginning to spread widely, and the rechargeable battery of high energy density is demanded as a power supply of these mobile computing devices. Especially, since a nonaqueous electrolyte rechargeable battery can expect the high tension more than the conventional nickel-ccadomium battery or a nickel hydoride battery, it craves for it noting that it is the power supply which can expect the further miniaturization of a device, and lightweight-ization. However, in the nonaqueous electrolyte rechargeable battery using the lithium metal and the lithium alloy as a negative-electrode material, when charge and discharge were repeated, the arborescence projection of a lithium was formed on the negative electrode, and the cycle engine performance did not fall and it was not easily put in practical use by the reasons of a problem being in the reliability under an elevated temperature.
[0002] Since the carbon material as a negative-electrode active material which can occlusion emit a lithium, and the nonaqueous electrolyte rechargeable battery (the patent No. 1989293 description) using the multiple oxide of the lithium and transition metals which have the layer structure as positive active material are invented as a means to solve these troubles and it has the voltage beyond 4V in the state of charge, it spreads increasingly widely as a power supply of mobile computing devices. However, the current nonaqueous electrolyte rechargeable battery is expensive from containing cobalt in the large quantity, and the limit was in low-pricing as a power supply. For this reason, the attempt which replaces cobalt from nickel or manganese is active. Especially the manganese with a price cheap also in transition metals is most expected as what can replace cobalt. However, in order that the cycle engine performance may be worsened and the lithium manganic acid ghost of stoichiometric composition may improve this, other transition metals, such as cobalt, replace manganese (for example, the patent No. 2058834 description), or replacing some manganese with a lithium, as shown in JP,5-205744,A etc. is proposed.
[0003] However, since cobalt with a high price is used, replacing some manganese with cobalt etc. has a limit in low-pricing. Moreover, the conventional synthetic method of the lithium manganic acid ghost which replaced some manganese with the lithium mixes Mn raw material and Li raw material at a desired rate, and obtained by the about 600-degree C thing comparatively heat-treated at low temperature. Since it was heat-treated at low temperature, crystallinity did not become high, but these had the trouble that the reversible capacitance near about 4v fell to the oxidation-reduction potential of a pair lithium metal as the result. Furthermore, since crystallinity was low, at the temperature beyond a room temperature, there was a trouble that the internal impedance of a cell increased without the ability preventing the elution of manganese enough. moreover -- if it heat-treats at an elevated temperature 600

degrees C or more -- Li_2MnO_3 etc. -- since it was easy to generate a subphase and the manganese of the amount of requests and the substitute of a lithium did not take place, when were left at a temperature too higher than a room temperature, and the elution of manganese happened and it saved under the elevated temperature, there was a problem that the internal impedance of a cell will increase.

[0004]

[Problem(s) to be Solved by the Invention] Still, the lithium manganic acid ghost which replaced some manganese with the lithium is not enough, although there is a fixed effect in prevention of the increment in the internal impedance near a room temperature. Furthermore, under the severe condition, the elution of manganese still happened and it had the trouble that the internal impedance increased and the capacity of a cell fell rather than the temperature at the time of conservation was high. Furthermore, the lithium manganic acid ghost which replaced some conventional manganese with the lithium had the trouble that crystallinity was low and capacity also fell greatly. The technical problem of this invention is using a crystalline good lithium manganic acid ghost, and is to offer the nonaqueous electrolyte rechargeable battery with a good conservation property which a manganese elution does not happen and the internal impedance of a cell does not increase at the temperature beyond a room temperature especially, either, with high capacity maintained.

[Means for Solving the Problem] As a result of examining wholeheartedly how a lithium replaces some of heat treatment conditions of a spinel system lithium manganic acid ghost, and manganese, it found out that a lithium manganic acid ghost which has a specific X diffraction pattern was suitable especially as a positive-electrode material of a nonaqueous electrolyte rechargeable battery, and resulted in this invention.

[0005] For this invention, it sets to a nonaqueous electrolyte rechargeable battery equipped with a negative-electrode active material which can carry out occlusion bleedoff of the (1) lithium ion, and positive active material which consists of nonaqueous electrolyte of lithium ion conductivity, and a lithium content metallic oxide which can carry out occlusion bleedoff of the lithium ion; and said lithium content metallic oxide is general formula $Li[Li_X Mn_{2-X}]O_4$ (however, $0<=x<=0.18$).

In an X diffraction pattern which came out, is the lithium manganic acid ghost of a spinel system shown, and made Cu-K alpha 1 a line source It has at theta= 44.0**0.2 degrees (B). a diffraction peak -- at least 2 -- theta= 36.2**0.2 degrees (A) and 2 -- A nonaqueous electrolyte rechargeable battery with which half-value width of this X diffraction peak is 0.1**0.05 respectively, and the diffraction peak intensity ratio (B/A) is characterized by or more 0.9 being 1.3 or less, (2) A lattice constant of a spinel system lithium manganic acid ghost shown by general formula $Li[Li_X Mn_{2-X}]O_4$ (however, $0<=x<=0.18$) is related with 8.20A or more nonaqueous electrolyte rechargeable battery which is 8.24A or less.

[0006] Hereafter, this invention is explained concretely. A manganese raw material of a lithium manganic acid ghost used for this invention is EMD (Electolytic Manganese Dioxide), CMD (Chemical Manganese Dioxide), gamma-MnOOH, and $MnCO_3$ as an example. Although it can mention, it is EMD or $MnCO_3$. It is desirable. Moreover, although a lithium raw material can also mention Li_2CO_3, LiOH, LiCl, $LiNO_3$, Li_2SO_4, and CH_3COOLi as an example, it is Li_2CO_3. It is desirable. A lithium manganic acid ghost used for this invention will be created as follows, if an example is given. Li_2CO_3 is mixed with EMD ground so that mean particle diameter might be set to 5-25 micrometers so that a Mn/Li ratio may be set to 0.5, and it heat-treats at 800-900 degrees C among atmospheric air. Subsequently, it can obtain by cooling to a room temperature, adding $LiCO_3$, mixing like, to a desired Mn/Li ratio, and heat-treating 400-700 degrees C at 500-650 degrees C still more preferably. Unreacted Li_2CO_3 may remain with the second heat treatment being 400 degrees C or less, and it is not desirable. Moreover, since subphases, such as Li_2MnO_3, become is it easy to be compounded to be 700 degrees C or more, it is not desirable. If another example is given, after mixing $MnCO_3$ by which pulverization was carried out with grinders, such as a ball mill, and Li_2CO_3 by which pulverization was carried out similarly by desired Mn/Li ratio, it can obtain by heat-treating at 400-600 degrees C.

[0007] In replacing some manganese with a lithium, a lithium manganic acid ghost of this invention can make an intensity ratio (B/A) of an X diffraction peak 1.3 or less [0.9 or more]. The amount of substitute is chosen so that an intensity ratio of an X diffraction peak of a compounded lithium manganic

acid ghost may become the range of desired. For example, in performing heat treatment of 800 degrees C or more by using EMD as a start raw material, a peak intensity ratio becomes the range of desired in replacing more than 0.02 mol % of Mn by Li. Moreover, in heat-treating at about 400-degree C low temperature by using as a start raw material MnCO3 which carried out pulverization, even if it does not replace Mn, a peak intensity ratio becomes the range of desired. Therefore, it is desirable to replace Mn in [0-0.18 mol] %, and the further 0.02-0.18-mol range of % is desirable. Moreover, since it is alike, therefore charge-and-discharge capacity per unit weight decreases, a thing little as much as possible of the amount of substitute which the amount of substitute increases is desirable. Moreover, lowering of capacity becomes it large that the amount of substitute is more than 0.18 mol %, and it is not desirable.

[0008] Next, the measurement technique of an X diffraction pattern in this invention is explained. Measurement of an X diffraction pattern used RINT2500 made from Physical science Electrical and electric equipment. Cu-K alpha 1 (wavelength of 1.5405A) was used for X line source, and it carried out on the following device conditions. Tube voltage and current used a monochromator further respectively 50kV, 160mA, 0.5 degrees of divergent slits, a scattering slit of 0.5 degrees, and a light-receiving slit width of 0.15mm. Measurement was performed at part [for /], and scan speed scan step of 2 degrees 0.01 degree, and a scan shaft was performed on condition that 2 theta/theta. Moreover, half-value width lengthened the background from measured value of a diffraction pattern written with 2theta shafts, and made it width of a peak of height (h/2) of one half of diffraction peak intensity (h).

[0009] 2 to which a lithium manganic acid ghost compounded by the above technique originates a diffraction peak in a field at least (311) -- 2 originating in theta= 36.2**0.2 degrees (A) and (400) a field -- it has at theta= 44.0**0.2 degrees (B), and half-value width of this X diffraction peak is each 0.1**0.05, and the diffraction peak intensity ratio (B/A) is characterized by or more 0.9 being 1.3 or less. Since an elution of Mn happens that half-value width is 0.1**0.05 or more, it is not desirable. Moreover, even if half-value width is the aforementioned range, an elution of manganese tends to happen and a diffraction peak intensity ratio (B/A) is not desirable at less than 0.9. According to the simulation result by the lied belt method, although this reason is not necessarily clear, purity of a crystal is low, and when there is an oxygen defect, a peak intensity ratio falls. Therefore, since an average valence of manganese in a crystal falls and a content of unstable trivalent manganese increases more than a moiety, it is presumed that an elution of manganese happens. Moreover, lowering of charge-and-discharge capacity is not greatly desirable at 1.3 or more. Although this reason is not necessarily clear, either, if a lithium replaces manganese, according to the simulation result of the lied belt method, a peak intensity ratio will increase. Consequently, since a content of an increment, i.e., tetravalent manganese, increases, an average valence of manganese presumes that lowering of capacity becomes large.

[0010] LiMn 2O4 which is the conventional stoichiometric composition According to the JCPDS (The JointCommittee on Power Diffraction Standards) card 35-782, a lattice constant is 8.248A. A lattice constant of a lithium manganic acid ghost of this invention has 8.20A or more desirable 8.24A or less. Since a part of Mn in a crystal unit cell was replaced by Li with an ionic radius smaller than Mn, and/or since a reason nil why a lattice constant of a lithium manganic acid ghost of this invention is small has few oxygen defects, it is thought that it is because repulsion of Mn ion is suppressed. In 8.20A or less, capacity is remarkable and a lattice constant carries out below. This is considered to be because for an average valence of Mn to be too close to 4. Moreover, in 8.24A or more, an effect which replaced a part of Mn by Li is not acquired, but an elution of Mn happens, and cycle engine performance falls.

[0011] although it will not be limited as a negative-electrode material used for this invention especially if the occlusion bleedoff of the lithium can be carried out in an ionic state -- as an example -- metallic oxides, such as carbon materials, such as corks, a natural graphite, an artificial graphite, and difficulty graphitized carbon, and SiSnO, and LiCoN2 etc. -- although a metal nitride can be mentioned, it is a carbon material preferably. In this invention, when electrode-izing an active material, an electric conduction agent can be added if needed and it can fix to current collection material with a binder. As an example of an electric conduction agent, although a natural graphite, an artificial graphite, carbon black, KETCHIEN black, and acetylene black can be mentioned, concomitant use of a graphite or a graphite, and acetylene black is desirable. Although not limited especially as the addition, 1 - 20 % of the weight

is 3 - 10 % of the weight desirable still more preferably. If conductivity does not become homogeneity for it to be 1 or less % of the weight but it becomes 20% of the weight or more, capacity per unit volume will fall. moreover, to a binder, Pori ethylene tetrafluoride, polyvinylidene fluoride, an ethylene-propylene-diene terpolymer, a carboxymethyl cellulose, styrene butadiene rubber, a fluororubber, etc. are usually independent -- or although it is mixed and is used, it is not limited especially. As these additions, 1 - 20 % of the weight is 1 - 10 % of the weight desirable still more preferably. In 1 or less % of the weight, binding capacity is weak, at 20 % of the weight or more, migration of Li ion is checked and engine performance as a cell falls.

[0012] As the electrolytic solution, mixture made to dissolve this in various organic solvents is used by using lithium salt as an electrolyte. although not limited especially as an electrolyte -- LiClO4, LiBF4, LiPF6, LiAsF6, and LiCF3 SO3 etc. -- independent or mixture can be used. Moreover, although not limited especially as an organic solvent, if it illustrates, independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, gamma-butyrolactone, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, and a tetrahydrofuran, can be used.

[0013]

[Example] Hereafter, although this invention is explained to details using a concrete example, this invention is not limited to these examples.

(Example 1) It is [EMD with a mean particle diameter of 10 micrometers and] Li2 CO3 as a start raw material. After mixing by the presentation ratio of Li/Mn=0.51 (atomic ratio) and heat-treating at 850 degrees C among air for 40 hours, it applied for 20 hours and cooled to near a room temperature. the X diffraction pattern of this lithium manganic acid ghost -- Li2 MnO3 Mn 2O3 and Mn 3O4 etc. -- the diffraction peak which is a single spinel phase without the peak of a subphase, and originates in a field (311) and (400) a field -- each 2 -- having [and] at theta= 36.08 degrees and 2theta=43.86 degree, that half-value width was each 0.118 and 0.165. Moreover, the intensity ratio of the diffraction peak resulting from a field (311) and (400) a field was 0.8.

[0014] The above-mentioned lithium manganic acid ghost and Li2 CO3 It mixed so that it might become the presentation ratio of Li/Mn=0.61 (atomic ratio), and the lithium manganic acid ghost of this invention was again obtained by heat-treating at 650 degrees C among air for 12 hours. the diffraction peak to which the X diffraction pattern of this lithium manganic acid ghost originates in a field (311) and a field (400) -- each 2 -- theta= 36.25 degrees and 2theta=44.07 degree -- having -- and that half-value width -- each 0.118 and 0.118 -- it is -- crystallinity -- high -- Mn 2O3 and Mn 3O4 And Li2 MnO3 etc. -- it was checked from not having the diffraction peak of a subphase that it is a single cubic spinel. Furthermore, the intensity ratio of the peak resulting from the above-mentioned (311) field and a field (400) was 1.02. Moreover, it was 8.215A when accuracy was asked for the lattice constant using Si used as the standard substance. the result of elemental analysis to Li[Li0.1 1 Mn1.8 9] O4 [furthermore,] it is -- things were checked.

[0015] The concrete cell creation in this invention is explained. After the above-mentioned lithium manganic acid ghost mixed the acetylene black 3 weight section and the lepidic form natural-graphite 3 weight section as an electric conduction agent to 100, the fluororubber was mixed at a rate of 3 weight sections to AUW, the partially aromatic solvent of the ethyl acetate/ethylcellosolve which is the solvent of a fluororubber was added, wet blending was performed, and it considered as the paste. Subsequently, this paste was applied to both sides of aluminium foil with a thickness of 20 micrometers it is thin to a positive-electrode charge collector at homogeneity, and after making it dry, the positive electrode band-like by carrying out pressing with a roller press machine was created. Next, to the mixture of the meso carbon fiber 95 weight section graphitized at 3000 degrees C, and the lepidic form natural-graphite 5 weight section, purified water was added as the carboxymethyl-cellulose 1 weight section, the styrene-butadiene-rubber 2 weight section, and a solvent, wet blending was performed, and it considered as the paste. Subsequently, this paste was applied to both sides of copper foil with a thickness of 12 micrometers it is thin to a negative-electrode charge collector at homogeneity, and after making it dry, the negative electrode band-like by carrying out pressing with a roller press machine was created. Furthermore, it considered as the roll-like object by winding in the shape of a roll on both sides of the

polyethylene fine porous membrane of 25-micrometer thickness as a separator between the above-mentioned positive electrode and the above-mentioned negative electrode.

[0016] The insulating film was inserted in the pars basilaris ossis occipitalis of an iron cylinder can which performed nickel plating, and said roll-like object was inserted. Subsequently, the negative-electrode tab picked out from the roll-like object was welded to the can bottom, and the positive-electrode tab was welded to the gasket, the explosion-proof disk, and the lock out lid that consists of a PTC element. It is LiPF6 at the concentration of one mol/l. to the mixed solvent of ethylene carbonate and diethyl carbonate in a cell can. After pouring in the dissolved electrolytic solution and inserting an insulating film in the roll-like object upper part, said lock out lid was put in and the cylindrical nonaqueous electrolyte rechargeable battery with a 17mm height [of appearances] of 500mm was created by closing the edge of a cell can. (Example of a comparison) The nonaqueous electrolyte rechargeable battery was created like the example 1 except having used the lithium manganic acid ghost whose peak intensity ratio of the above-mentioned example 1 is 0.8.

[0017] (Example 2) The nonaqueous electrolyte rechargeable battery was created like the example 1 except having changed the synthesis method of a lithium manganic acid ghost as follows. It is MnCO3 of impalpable powder as a start raw material. Li2 CO3 By the presentation ratio of Li/Mn=0.51 (atomic ratio), it ground and mixed with the ball mill for 48 hours, and among air, it heat-treated at 800 degrees C for 20 hours, and the lithium manganic acid ghost of this invention was obtained by lowering the temperature to near a room temperature over 20 hours. It was the single cubic spinel which the X diffraction pattern of the obtained lithium manganic acid ghost has each diffraction peak which originates in a field and a field (400) at least (311) at 2theta=36.13 degree and 2theta=43.94 degree, and the half-value width is 0.106 and 0.118 respectively, and its crystallinity is high, and does not have the peak of a subphase. The peak intensity ratio of the aforementioned (311) field and a field (400) was 1.1. Moreover, it was 8.232A when accuracy was asked for the lattice constant using Si used as the standard substance. the result of elemental analysis to Li[Li0.0 1 Mn1.9 9]O4 [furthermore,] it is -- things were checked.

[0018] [Test result] It set charge voltage as 4.2V, and charged in 5 hours after each cell created in the above-mentioned examples 1 and 2 and the example of a comparison passed the aging period of 24 hours for the purpose of the stabilization inside a cell. Subsequently, it discharged to 2.7V with 500mA fixed current, the initial capacity of each cell was measured, and the capacity per unit positive-active-material weight in a cell was calculated. Subsequently, after setting charge voltage as 4.2V and charging in 3 hours, the alternating current impedance (X) in the frequency of 1kHz was measured, and it took out, 24 hours after putting a cell into the thermostat adjusted to 85 degrees C. The taken-out cell measured the alternating current impedance (Y) in the frequency of 1kHz, after being cooled naturally to near a room temperature. Based on these, the internal impedance rate of increase of the cell per unit time amount was computed according to the degree type.

[(Y-X) /X] The discharge capacity per unit positive active material and the impedance rate of increase per unit time amount which were computed from initial capacity and the impedance measurement result before and behind conservation are shown in /24x100 table 1.

[0019]

[A table 1]

表1

	初期放電量 (mAh/g)	インピーダンス増加率 (%/hr.)
実施例1	102	4.8
実施例2	126	5.7
比較例	123	17.6

Although the initial capacity of the cell of an example 1 is low compared with the example of a comparison as shown in a table 1, the impedance rate of increase is small. Although this has a small initial capacity since a part of manganese is replaced by the lithium, it is thought by the elution of manganese being prevented according to said effect, and it being that the rate of increase of internal impedance is small. On the other hand, the cell of an example 2 has a comparable initial capacity compared with the example of a comparison, and its impedance rate of increase is small. Since manganese is hardly replaced by the lithium, since there are few oxygen defects, this is considered that the rate of increase of internal impedance is small by the elution of manganese being prevented greatly [initial capacity].

[0020]

[Effect of the Invention] As explained above, set to the X diffraction pattern of this invention. a diffraction peak -- at least 2 -- theta= 36.2**0.2 degrees (A) and 2 -- even if saved at the elevated temperature beyond a room temperature in the nonaqueous electrolyte rechargeable battery for which it has at theta= 44.0**0.2 degrees (B), and the half-value width of this X diffraction peak is each 0.1**0.05, and the diffraction peak intensity ratio (B/A) used the or more 0.9 lithium manganic acid ghost of the spinel system it is [system] 1.3 or less, the rate of increase of the internal impedance of a cell is small. Furthermore, since other expensive elements are not used, it is cheap. Consequently, a nonaqueous electrolyte rechargeable battery without the case where used the lithium manganic acid ghost of a cheap material, and an expensive lithium cobalt oxide is used, and inferiority can be offered. A highly efficient nonaqueous electrolyte rechargeable battery can be cheap, it can supply now, and the industrial value is large.

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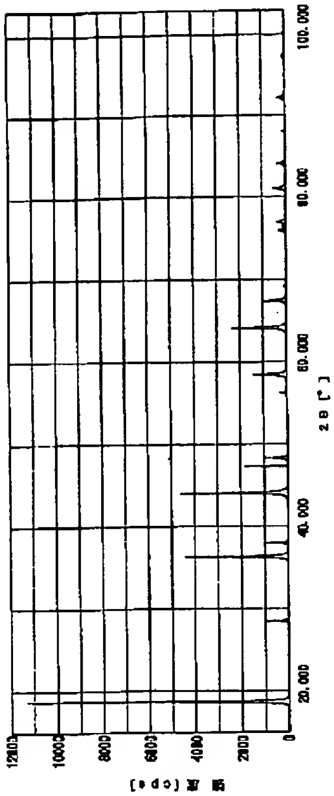
Drawing selection Representative drawing



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